HIGH ENERGY DENSITY CATHODES FOR NEXT GENERATION LITHIUM ION BATTERIES

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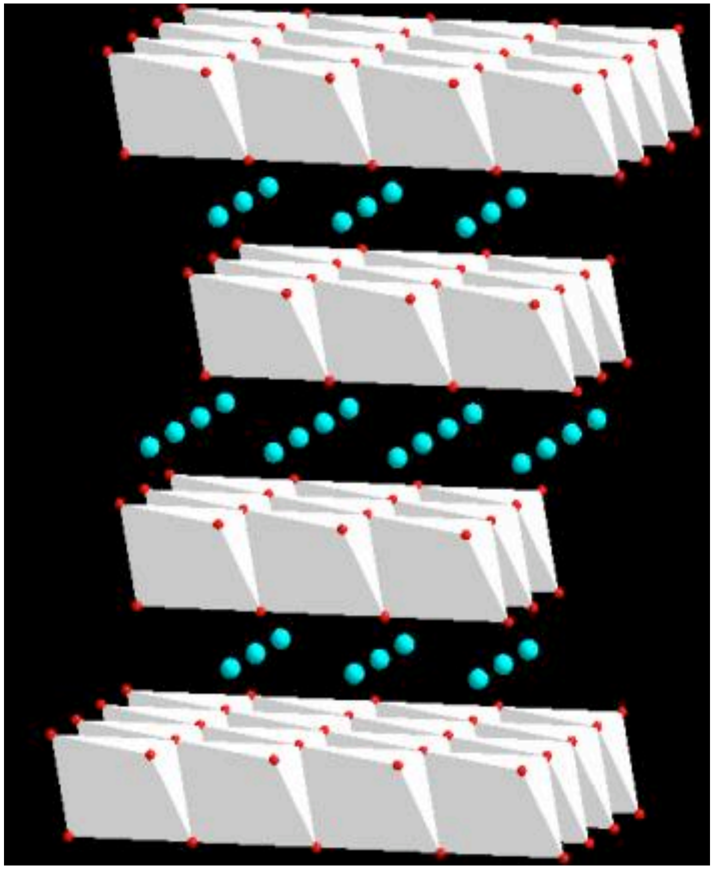
LAYERED $Li[Li_{1/3}Mn_{2/3}]O_2$ - $Li[Mn_{1-y-z}Ni_yCo_z]O_2$ SYSTEM



$(Li,Mn,Ni,Co)O_2$

Li^+

$(Li,Mn,Ni,Co)O_2$

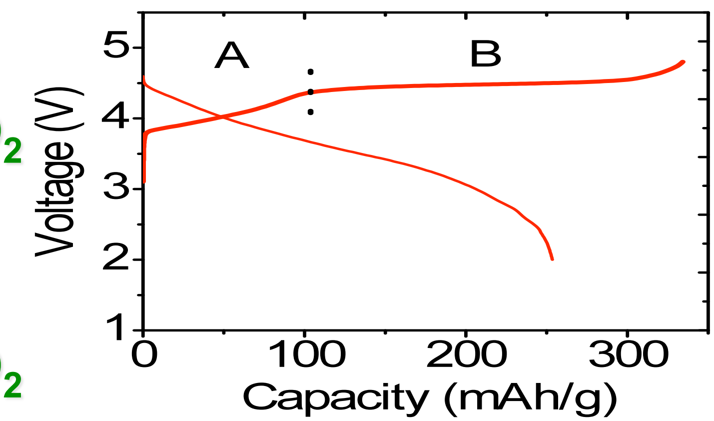
Li^+

$(Li,Mn,Ni,Co)O_2$

Li^+

$(Li,Mn,Ni,Co)O_2$

$Li[Li_{1/3}Mn_{2/3}]O_2 = Li_2MnO_3$



Region A: Oxidation of $M^{2+/3+}$ to M^{4+}
Region B: Oxidation of O^{2-} to O

- Higher capacity (~ 300 mAh/g), lower cost, and better safety than $LiCoO_2$
- Lose oxygen from the lattice during first charge, needs charging to 4.8 V
- High irreversible capacity loss (40 – 100 mAh/g) during first cycle
- Low rate capability, low tap density

OUTLINE

- Reducing irreversible capacity loss and increasing discharge capacity

  - by surface modification and the mechanism
  - by incorporating lithium-free insertion hosts

- Enhancing the rate capability
- - by reducing SEI layer thickness through surface modification

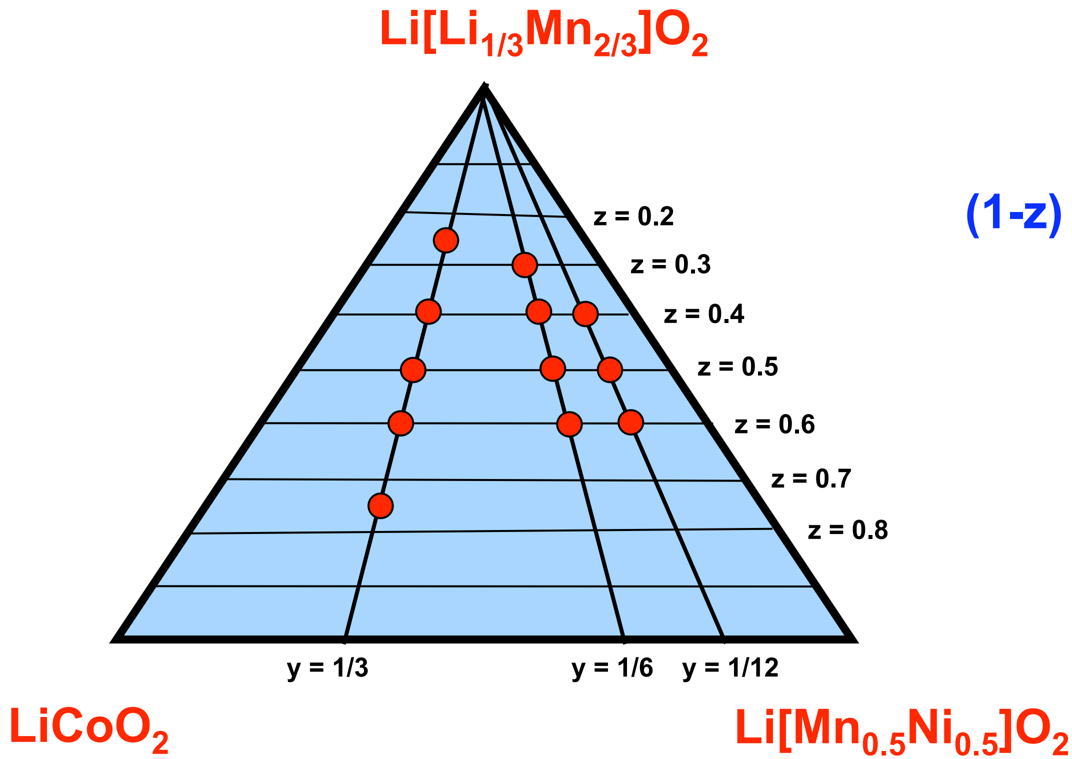
- Increasing the tap density and scale up

- Conclusions

REDUCING THE IRREVERSIBLE CAPACITY LOSS

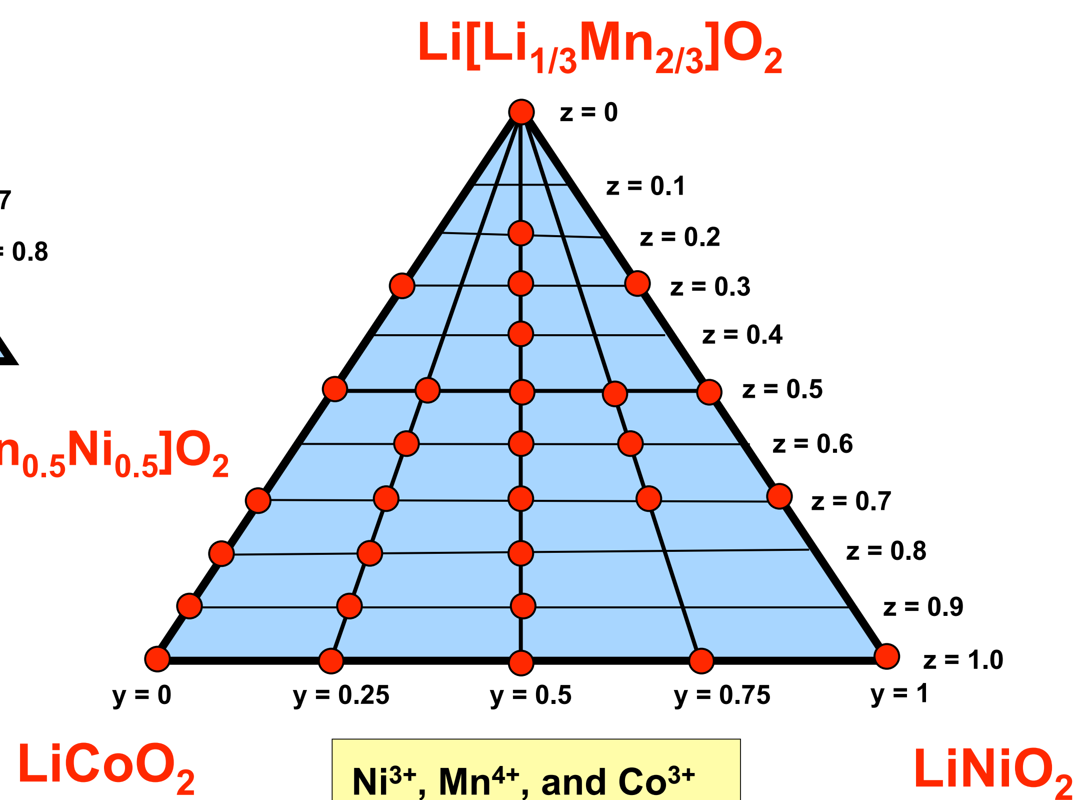
PHASE DIAGRAMS OF SYSTEMS INVESTIGATED

$(1\text{-}z)\ Li[Li_{1/3}Mn_{2/3}]O_2 - (z)\ Li[Mn_{0.5-y}Ni_{0.5-y}Co_{2y}]O_2$



Ni^{2+}, Mn^{4+}, and Co^{3+}

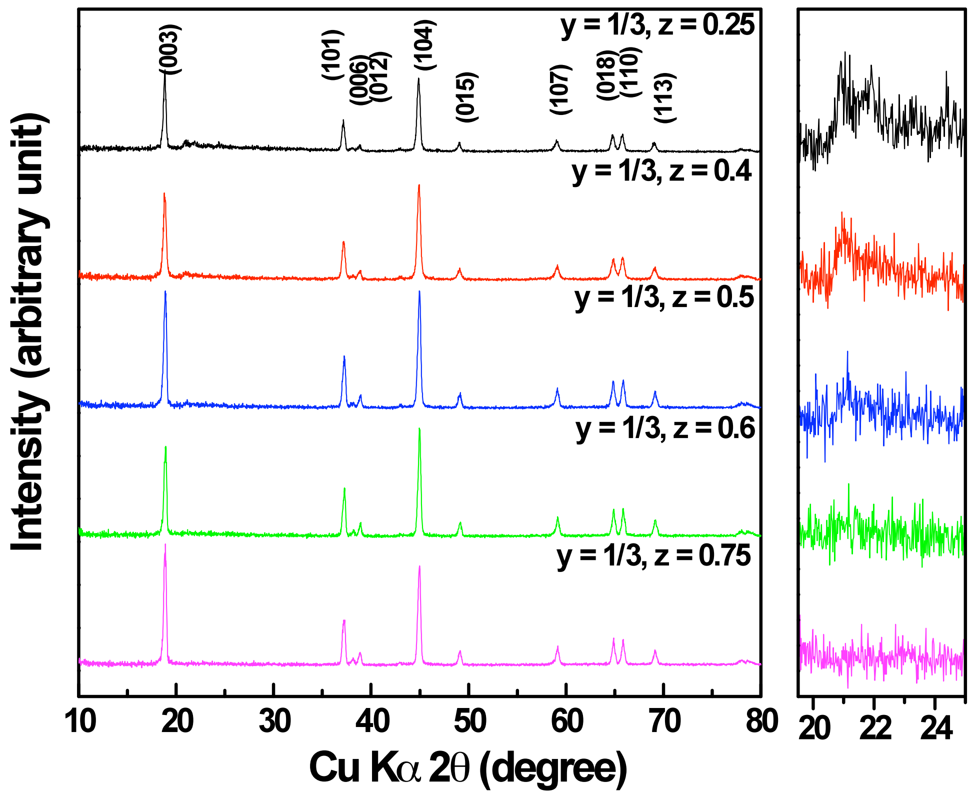
$(1\text{-}z)\ Li[Li_{1/3}Mn_{2/3}]O_2 \cdot (z)\ Li[Ni_{1-y}Co_y]O_2$



Ni^{3+}, Mn^{4+}, and Co^{3+}

XRD PATTERNS OF (1-z) $Li[Li_{1/3}Mn_{2/3}]O_2$ – (z) $Li[Mn_{0.5-y}Ni_{0.5-y}Co_{2y}]O_2$

(1-z) $Li[Li_{1/3}Mn_{2/3}]O_2$ – (z) $Li[Mn_{1/6}Ni_{1/6}Co_{2/3}]O_2$



- All materials show single O3 type phase similar to $LiCoO_2$
- Weak reflections around 2θ = 20 - 25° are due to the ordering of the Li^+ and Mn^{4+} ions in the transition metal layer or Li_2MnO_3 clustering

SURFACE MODIFICATION WITH AUMINUM OXIDE

Aluminum nitrate, Al $(NO_3)_2 \cdot 9\ H_2O$

Layered oxide

Ammonium hydroxide (NH_4OH)

Aluminum hydroxide + layered oxide slurry

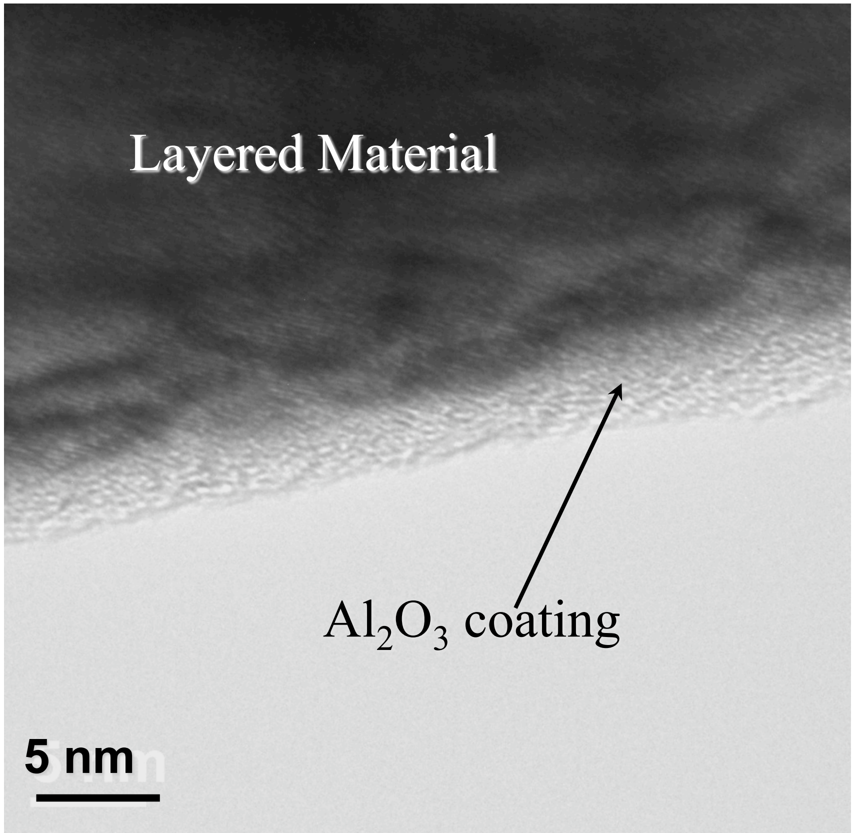
The weight ratio of layered oxide and Al_2O_3 is 97:3

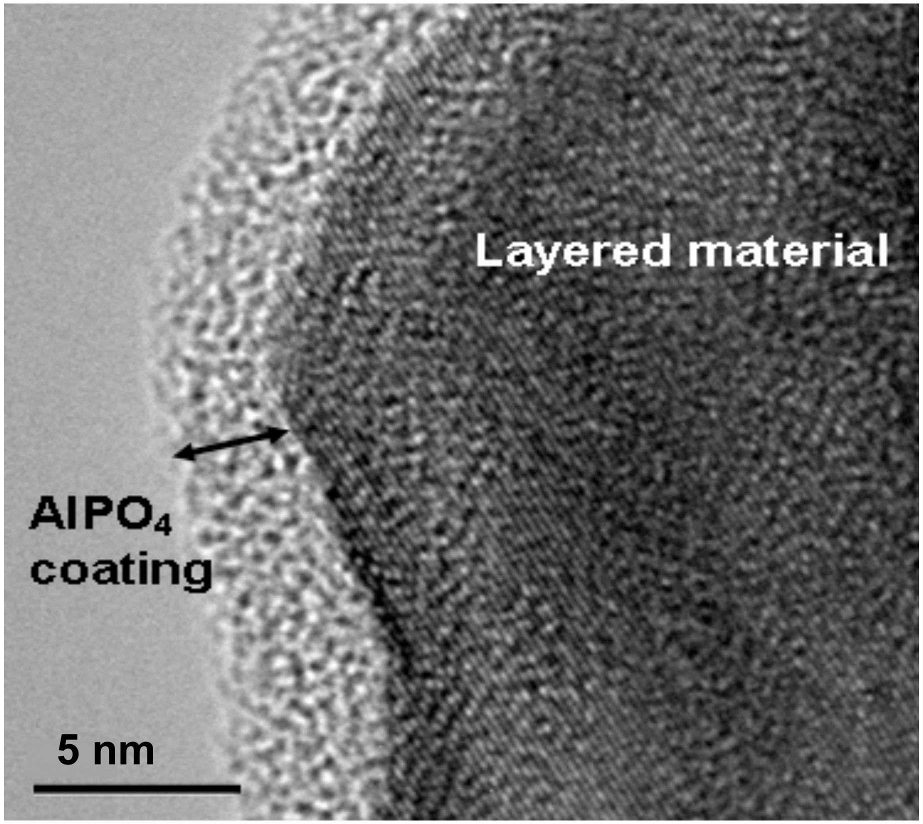
Slurry was filtered and dried in an oven at 100 ^oC for 12 h

Annealed at 300 ^oC for 5 h

Layered oxide coated with "Al_2O_3"

SURFACE MODIFIED $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$



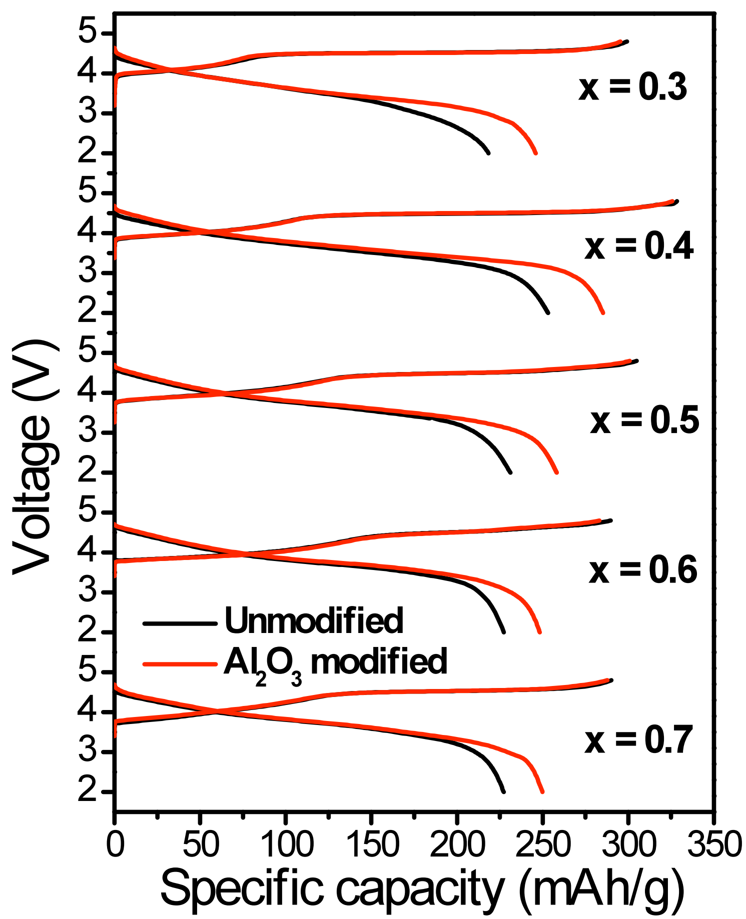


Y. Wu, A. Vadivel Murugan, and A. Manthiram, *J. Electrochem. Soc.* **155**, A635 (2008).

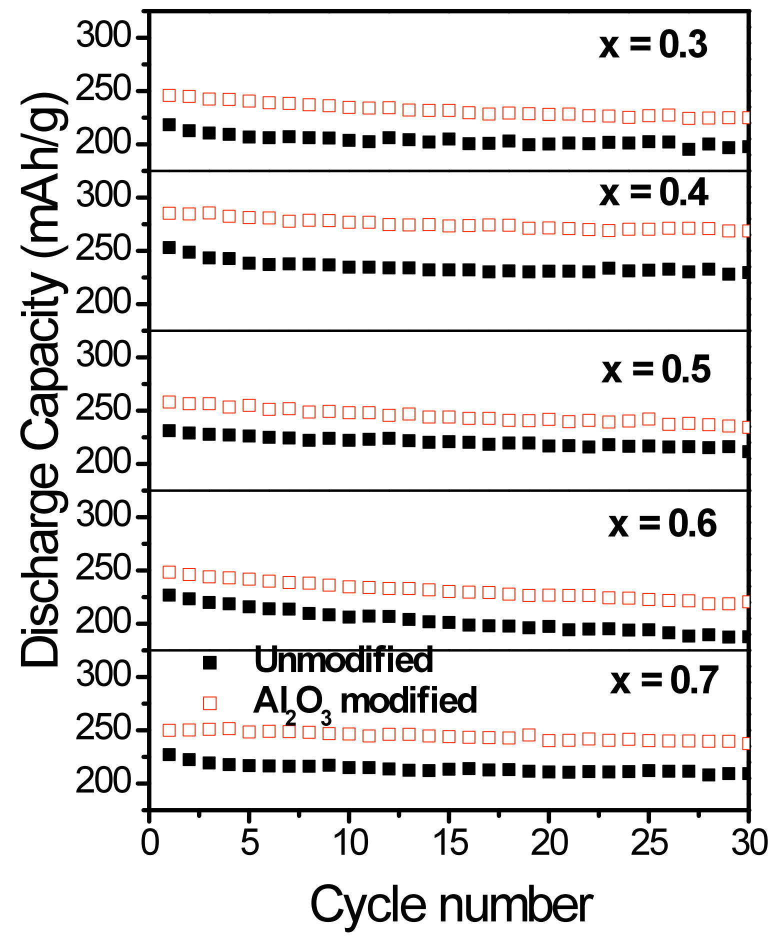
- A smooth, porous layer with a thickness of ~ 5 nm exists on the surface
- EDS analysis indicates aluminum and phosphorous on the surface

HIGH CAPACITY (1-x) $Li[Li_{1/3}Mn_{2/3}]O_2$ – x $Li[Mn_{1/3}Ni_{1/3}Co_{1/3}]O_2$

First Cycle



Cyclability



Y. Wu and A. Manthiram, *Electrochem. Solid State Lett.* **9**, A221 (2006).

- Surface modification reduces irreversible capacity & increases reversible capacity
- Discharge capacity is maximized at an intermediate Li_2MnO_3 content (1-x = 0.6)

ORIGIN OF IRREVERSIBLE CAPACITY LOSS

Armstrong et al. *J. Am. Chem. Soc., 128, 8694 (2006)*

Based on electrochemical mass spectroscopy & powder neutron diffraction *of*

$Li[Li_{0.2}Mn_{0.6}Ni_{0.2}]O_2$: $0.6\ Li[Li_{1/3}Mn_{2/3}]O_2 - 0.4\ Li[Mn_{0.5}Ni_{0.5}]O_2$

$\mathbf{Li[Li_{0.2}M_{0.8}]O_2}$

↓ **Oxidation of $M^{2+/3+}$ to M^{4+} (region A)**

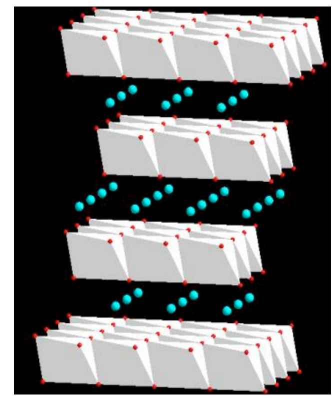
$\mathbf{Li_{0.6}\square_{0.4}[Li_{0.2}M_{0.8}]O_2}$

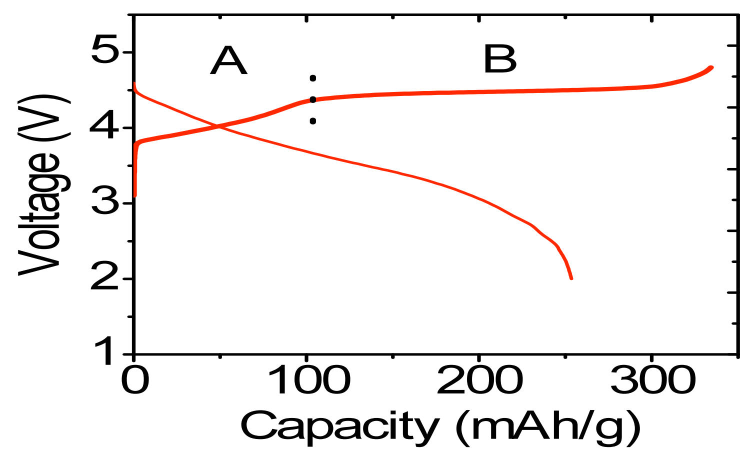
↓ **Oxidation of O^{2-} to O (region B)**
Migration of Li^+ from TM layer to Li layer

$\mathbf{\square_{1.0}[\square_{0.2}M_{0.8}]O_{1.6}\square_{0.4}}$

↓ **Elimination of O^{2-} & Li^+ vacancies**
Diffusion of M^{4+} from surface to bulk

$\mathbf{[M_{0.8}]O_{1.6}}$ (*i.e.* $\mathbf{0.8[M]O_2}$ or $\mathbf{0.8\square_{1.0}[M]O_2}$)





- 1.2 Li^+ extracted during 1st charge
- 0.8 Li^+ inserted during 1st discharge

ANALYSIS OF CHARGE-DISCHARGE CAPACITY VALUES

$Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$

Parameter	Experimental (mAh/g)	All oxide ion vacancies eliminated	All oxide ion vacancies retained in the lattice
First charge capacity (mAh/g)	328	328	328
First discharge capacity (mAh/g)	253	217	328
Irreversible capacity loss (mAh/g)	75	111	0

Y. Wu, A. Vadivel Murugan, and A. Manthiram, *J. Electrochem. Soc.* **155**, A635 (2008).

- Part of the oxide ion vacancies is retained in the lattice
  - 66 % vacancies eliminated and 34 % retained in the lattice

SURFACE MODIFIED $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$

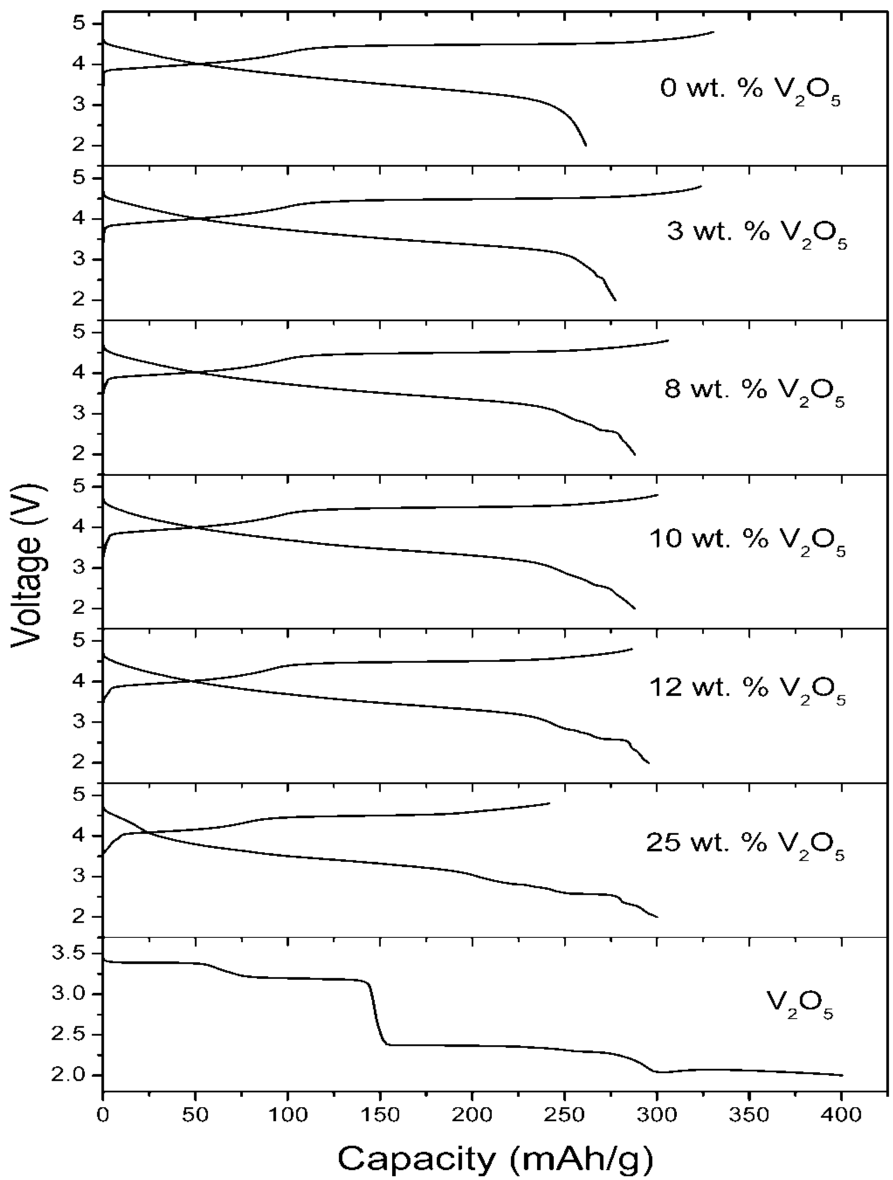
Modified By	1st charge Capacity (mAh/g)	1st discharge capacity (mAh/g)	IRC (mAh/g)	Theoretical discharge capacity* (mAh/g)	Theoretical IRC*(mAh/g)	Composition after 1st charge based on observed discharge Capacity	% oxide ion vacancy retention
Pristine	328	253	75	217	111	$Li_{0.075}[Li_{0.085}M_{0.8}]O_{1.65}\square_{0.12}$	34
Al_2O_3	326	285	41	217	128	$Li_{0.025}[Li_{0.135}M_{0.8}]O_{1.65}\square_{0.22}$	63
CeO_2	289	253	36	198	91	$Li_{0.135}[Li_{0.145}M_{0.8}]O_{1.71}\square_{0.18}$	62
ZrO_2	300	252	48	204	96	$Li_{0.12}[Li_{0.12}M_{0.8}]O_{1.69}\square_{0.15}$	48
ZnO	310	252	58	209	101	$Li_{0.105}[Li_{0.105}M_{0.8}]O_{1.68}\square_{0.13}$	41
$AlPO_4$	283	261	22	195	88	$Li_{0.135}[Li_{0.165}M_{0.8}]O_{1.72}\square_{0.21}$	75
F^-	328	270	58	217	111	$Li_{0.05}[Li_{0.11}M_{0.8}]O_{1.65}\square_{0.17}$	49

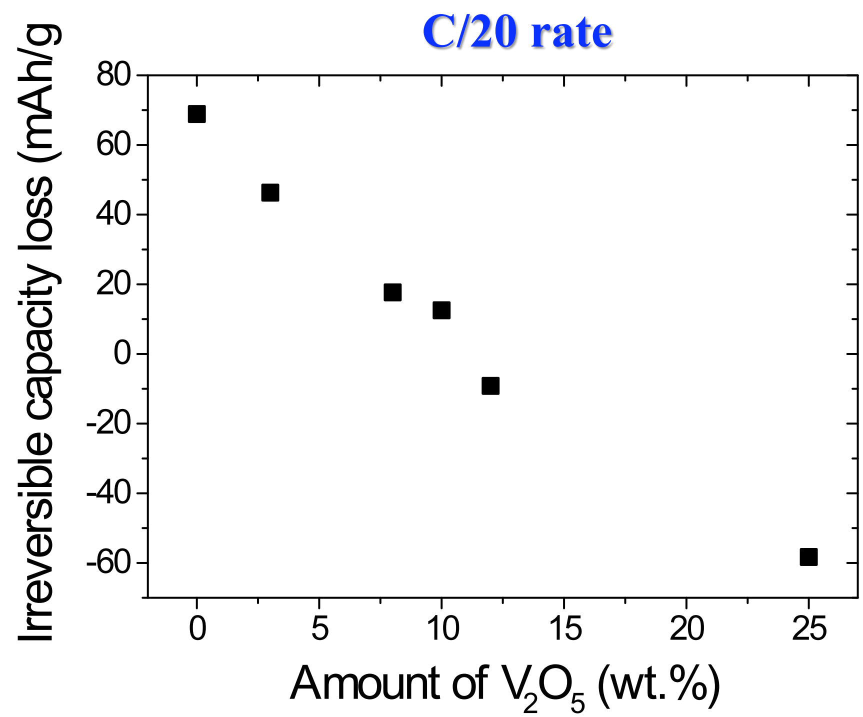
*** Calculated assuming all the oxide ion vacancies are eliminated**

Y. Wu and A. Manthiram, *Solid State Ionics* **180**, 50 (2009)

- **The retention of oxide ion vacancies occurs to a greater extent on surface modified samples.**

LAYERED $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2 + V_2O_5$ COMPOSITE



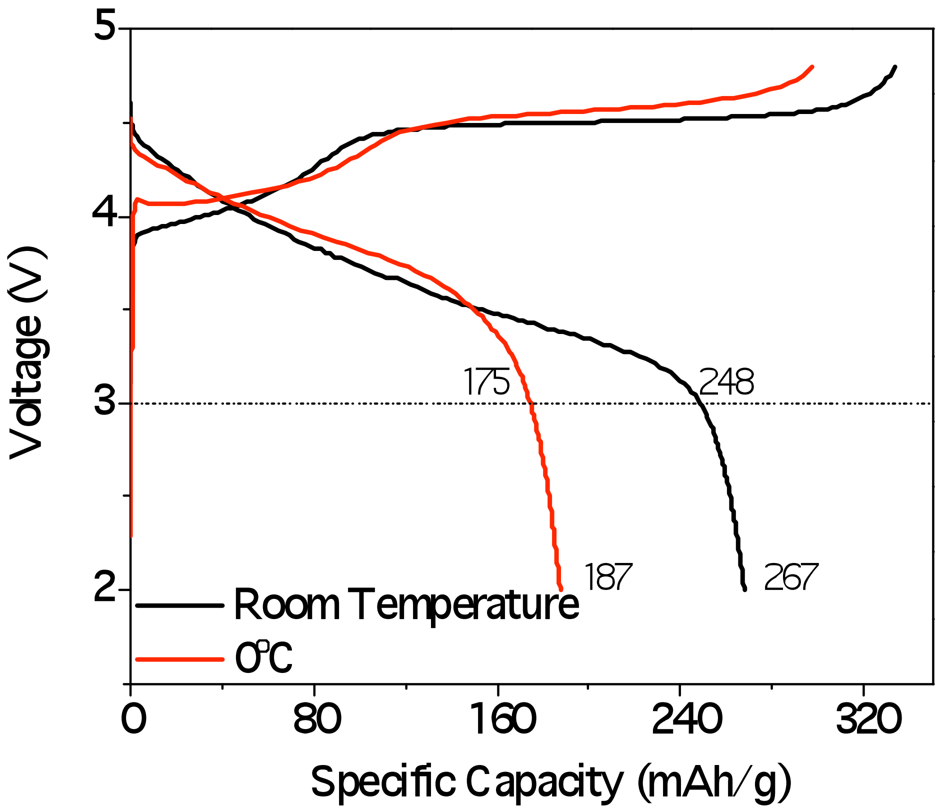


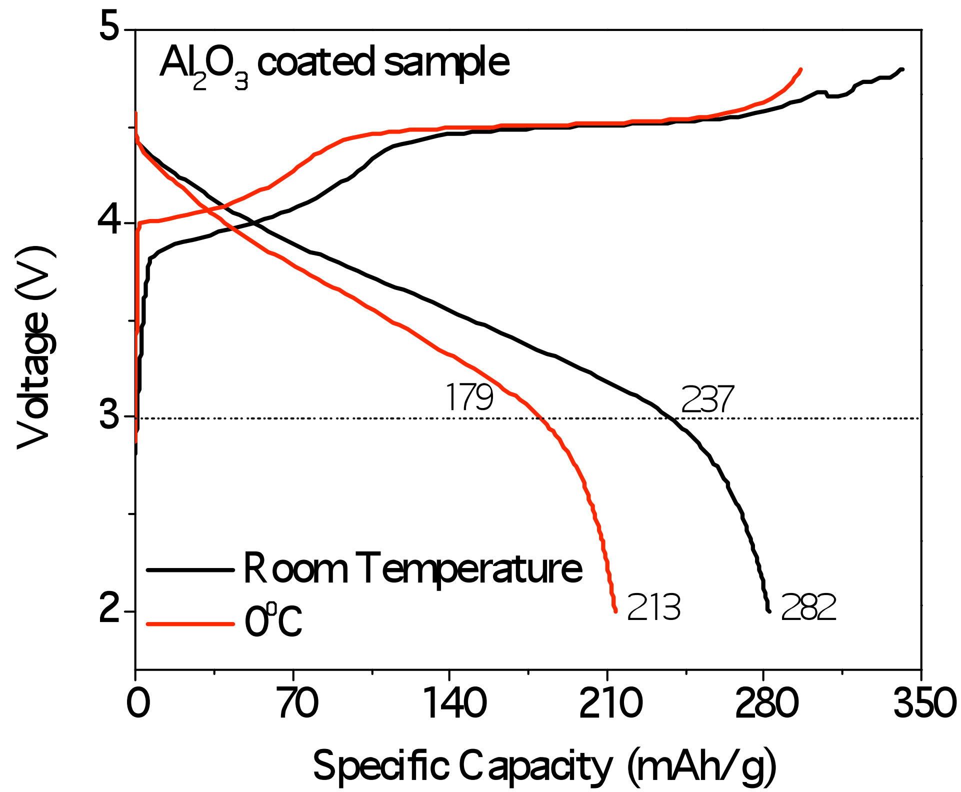
- Addition of the lithium-free V_2O_5 host provides the sites for inserting back the lithium ions that could not be put back into the layered lattice and thereby reduces the irreversible capacity loss and increases the discharge capacity

J. Gao, J. Kim, and A. Manthiram, *Electrochem. Commun.* **11**, 84 (2009)

ENHANCING THE RATE CAPABILITY

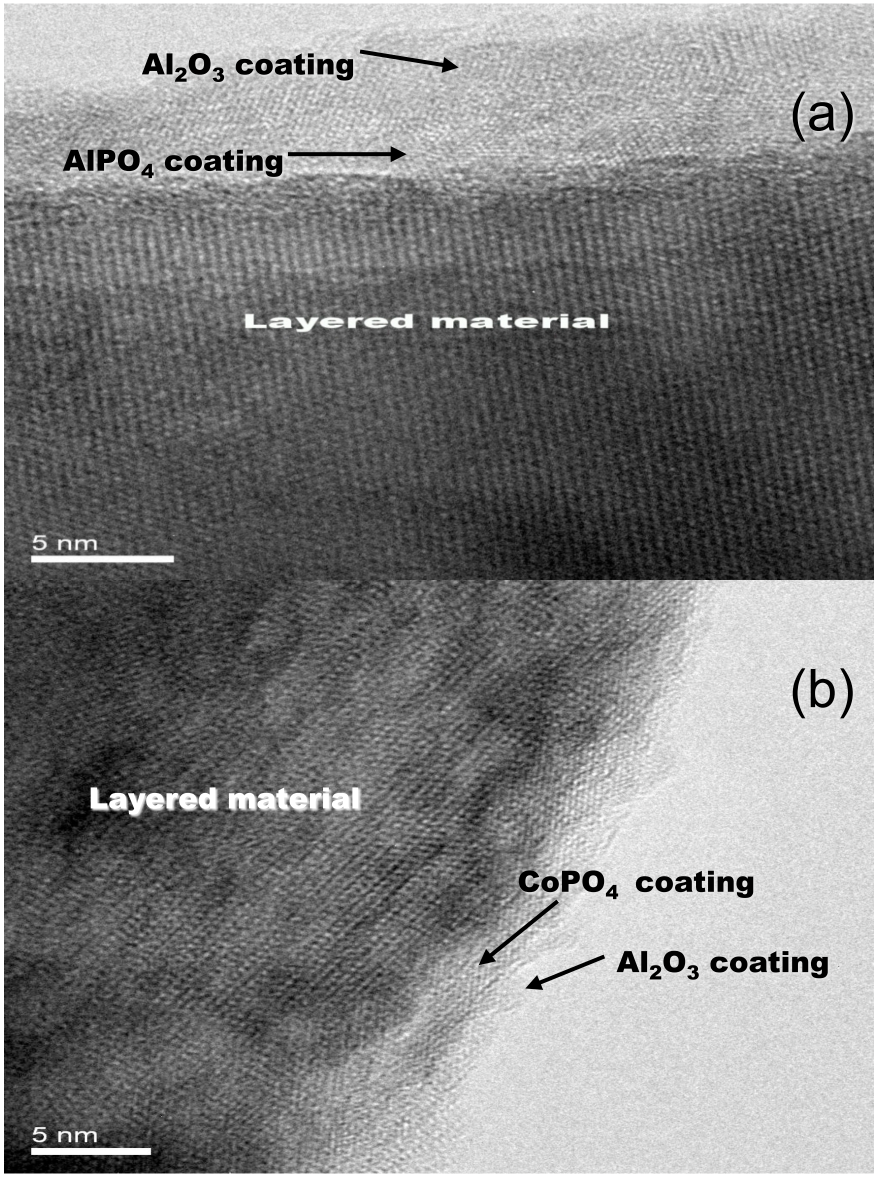
LOW TEMPERATURE PERFORMANCE AT C/10 RATE



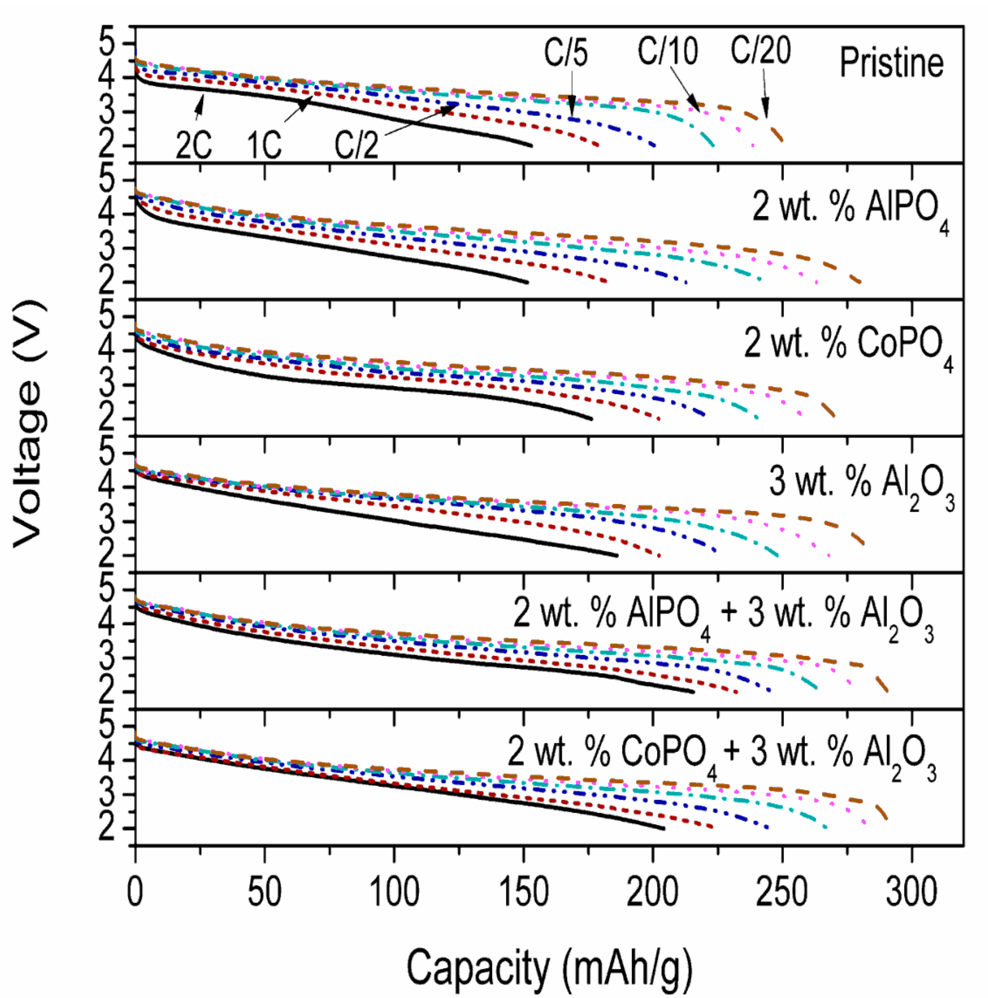


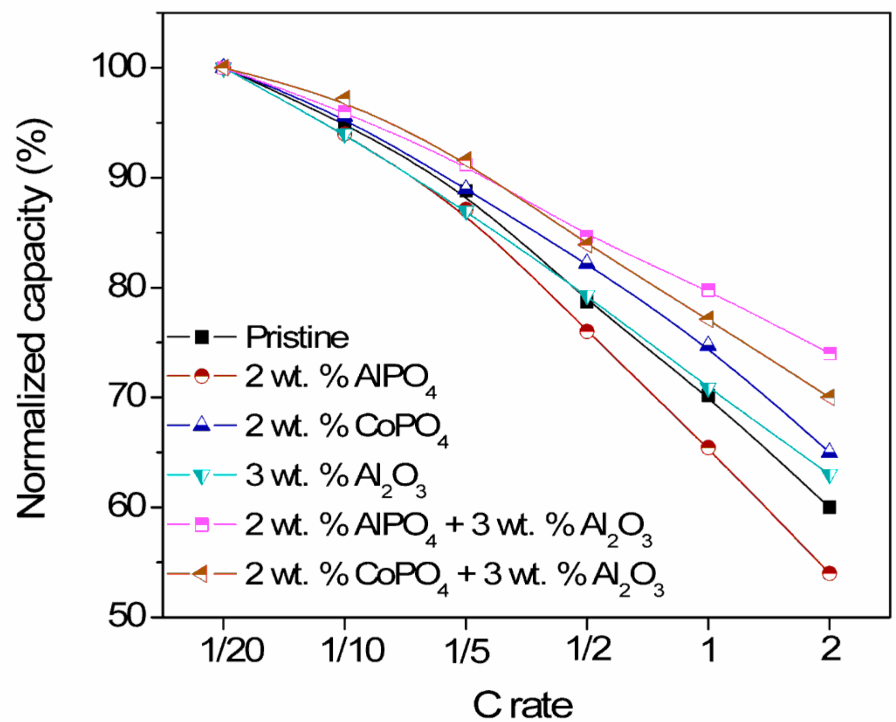
- Surface modification enhances the low temperature performance
  - **Pristine sample:** 70 % of the capacity retained at 0 °C
  - **Al_2O_3-coated sample:** 75 % of the capacity retained at 0 °C

DOUBLE LAYERED COATED $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$



RATE CAPABILITIES OF $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$

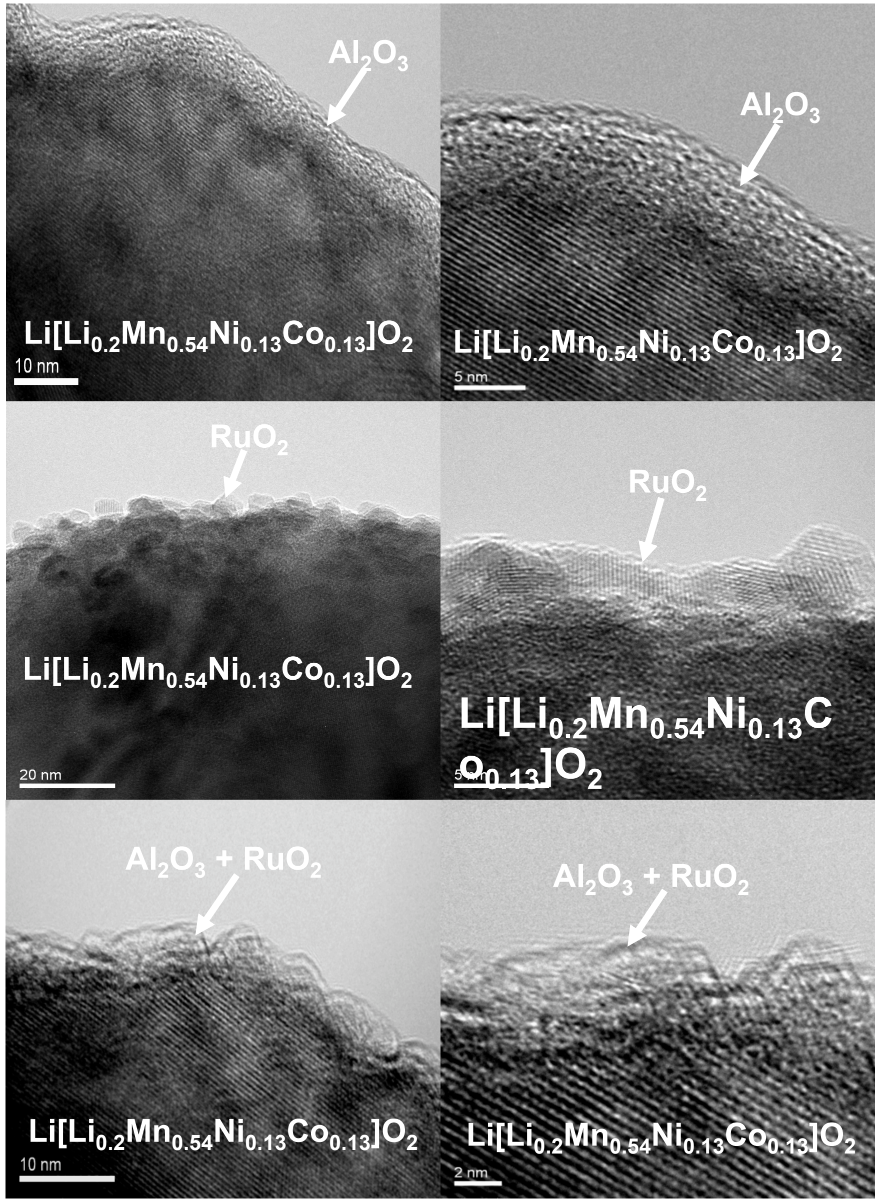




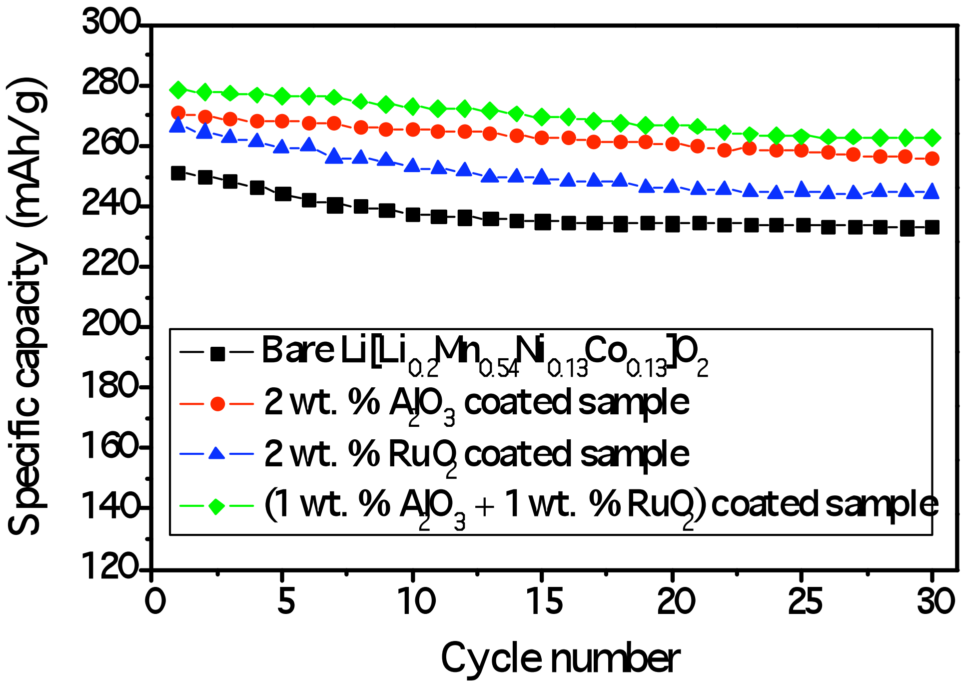
Q. Wang, J. Liu, A. Vadivel Murugan, and A. Manthiram, *J. Mat. Chem.* **19**, 4965 (2009)

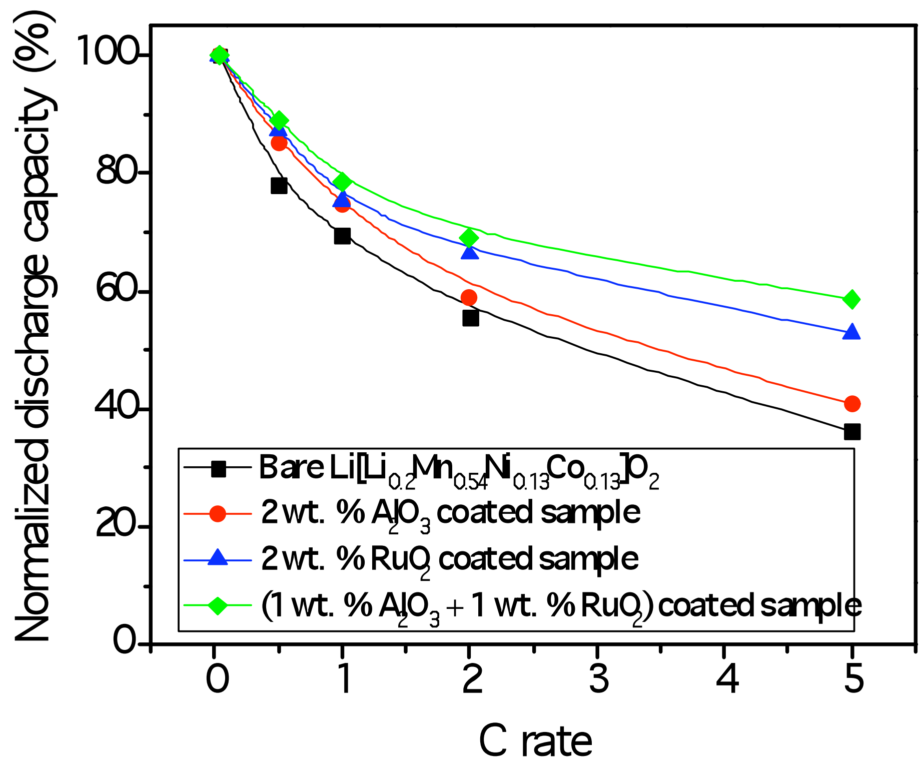
- Double-layer coated samples exhibit higher rate capability than pristine and single-layer coated samples due to the suppression of SEI layer formation

SURFACE MODIFIED $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$



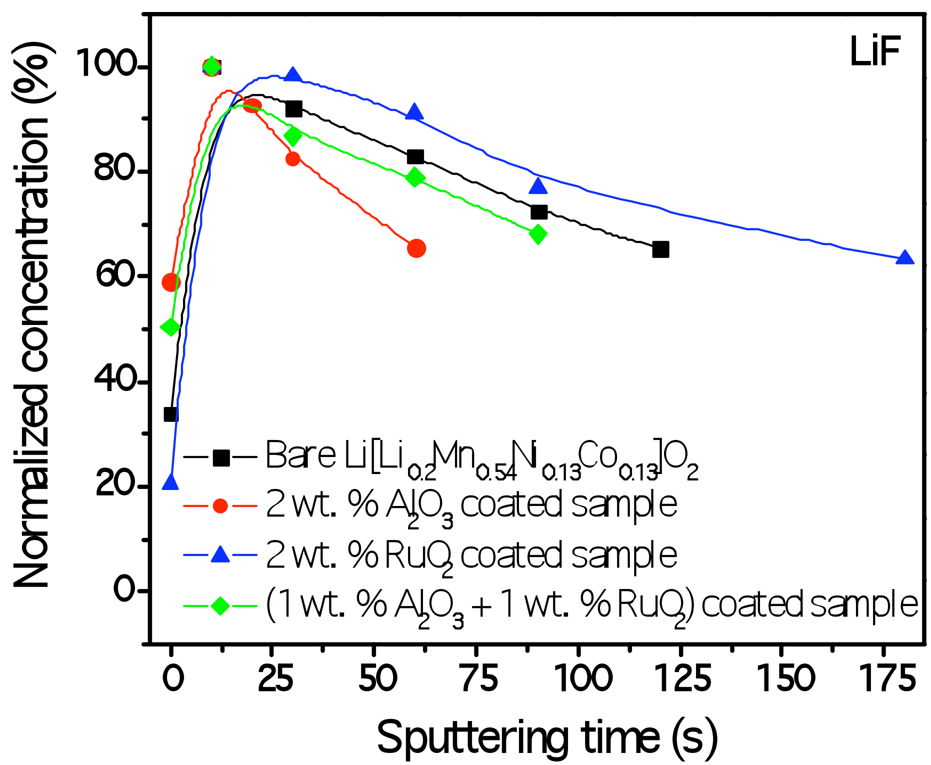
CYCLABILITY AND RATE CAPABILITY OF $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$

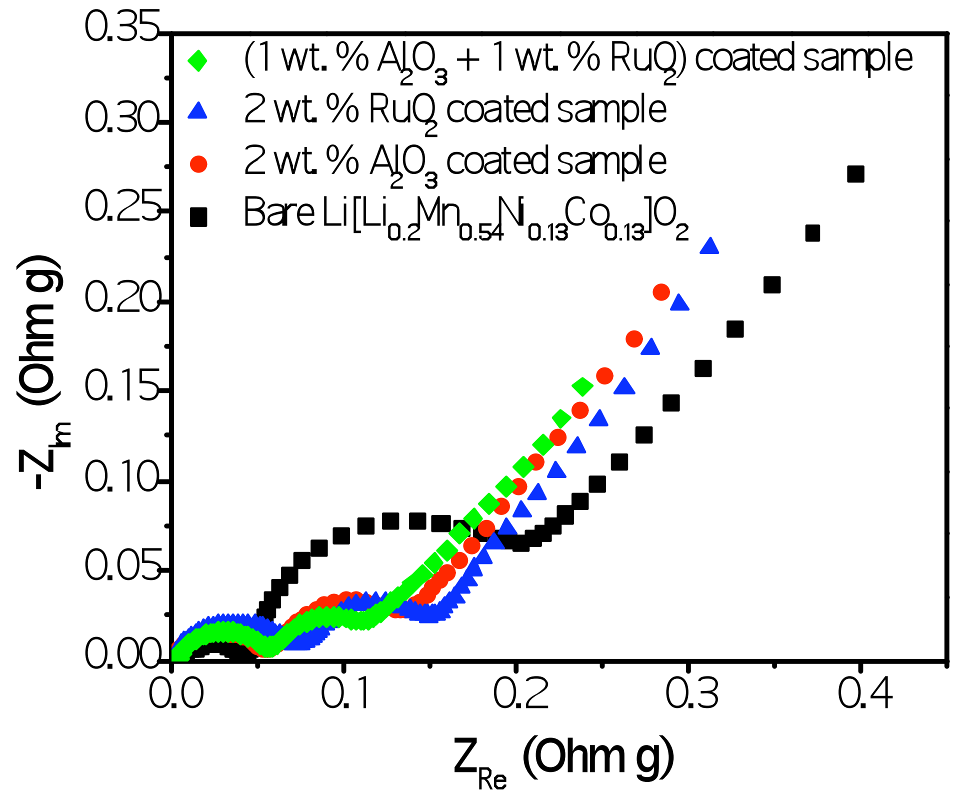




- Double-layer coated samples exhibit higher rate capability than pristine and single-layer coated samples due to the suppression of SEI layer formation and the facilitation of ionic and electronic diffusion channels

DEPTH PROFILE ANALYSIS OF SEI LAYER BY XPS AND EIS DATA

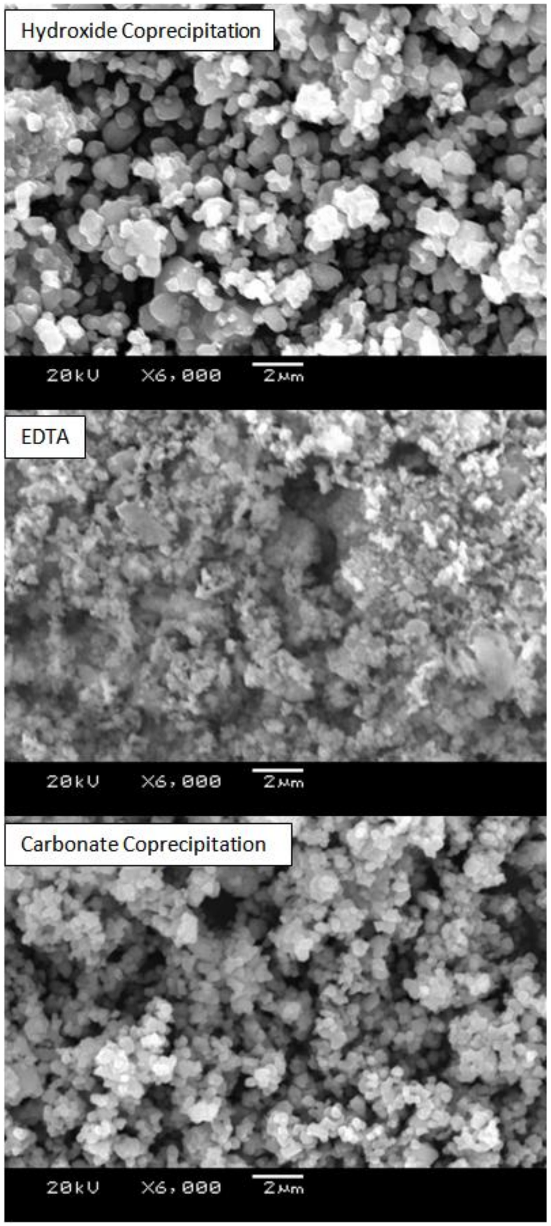




- The suppression of SEI layer formation and the facilitation of ionic and electronic diffusion channels in the Al_2O_3 + RuO_2 coated sample lead to lower charge transfer resistance and higher rate capability

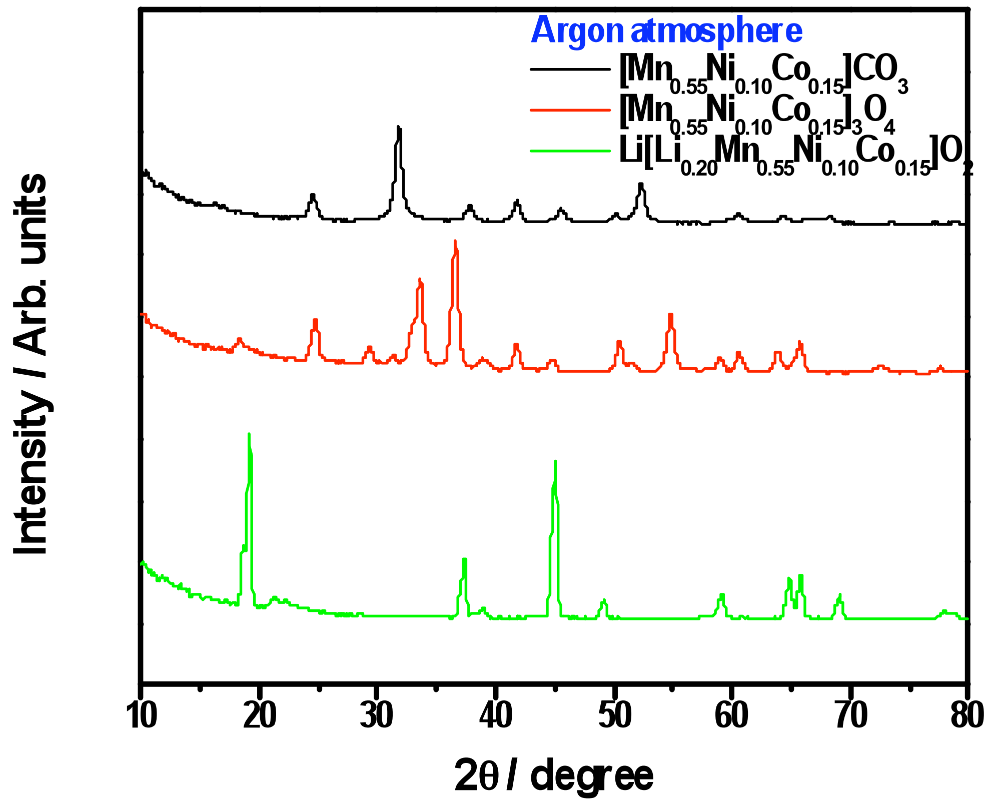
ENHANCING THE TAP DENSITY AND SCALE UP

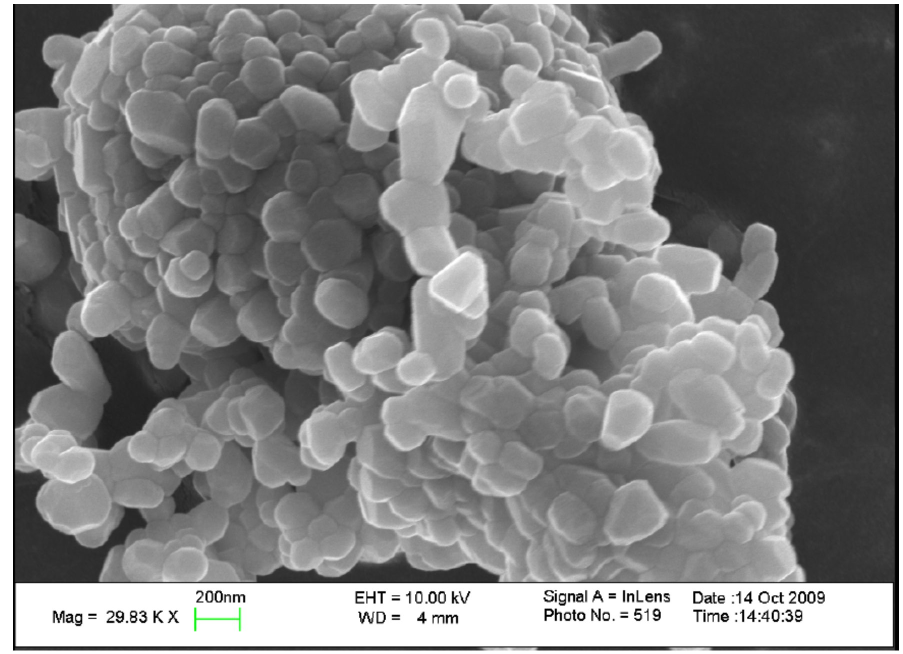
INFLUENCE OF SYNTHESIS METHOD



- Synthesis method influences morphology
- Morphology influences
  - capacity values
  - cyclability
  - rate capability
  - tap density
- Hydroxide method is difficult to scale up as the properties vary from batch to batch

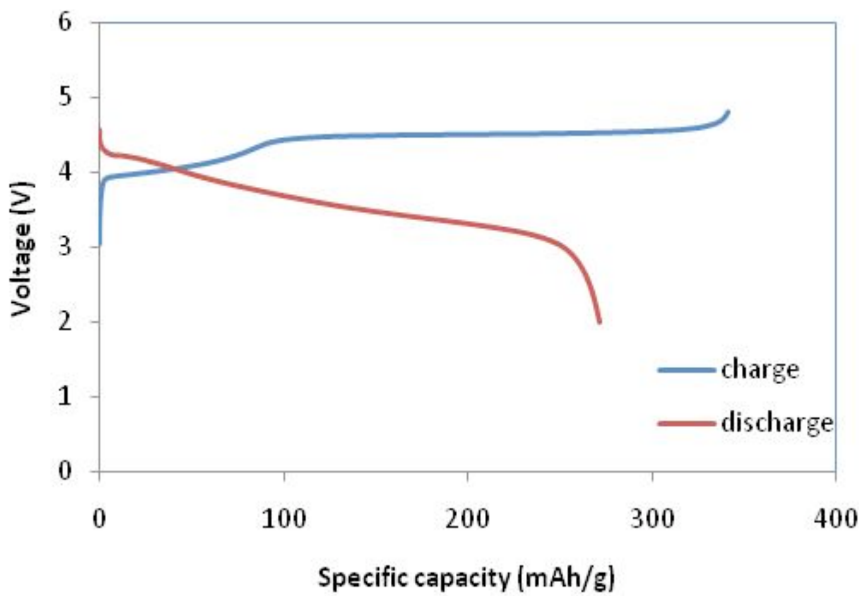
SYNTHESIS BY CARBONATE COPRECIPITATION METHOD

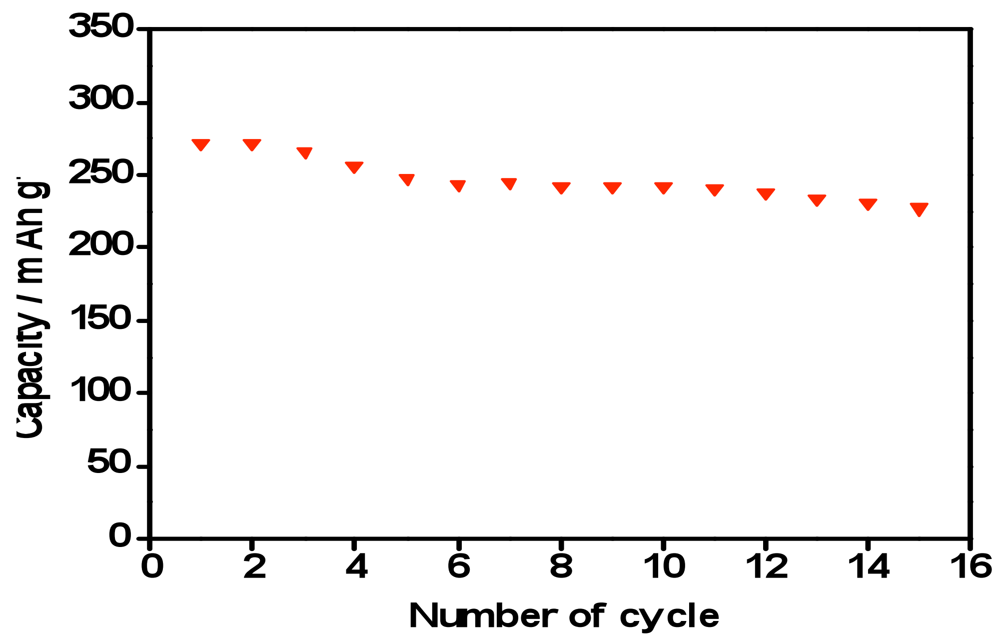




- Carbonate precursors are fired first to obtain the spinel oxide and then mixed with LiOH and fired to obtain the layered oxide
- Carbonate precursor offers better particle morphology and higher tap density compared to the EDTA and hydroxide coprecipitation

PERFORMANCE OF SAMPLES OBTAINED FROM CARBONATES





- Exhibit 270 mAh/g at C/10 rate at 4.8 – 2.0 V
- Surface modification could increase the capacity to close to 300 mAh/g

CONCLUSIONS

- Surface modified complex layered oxides offer ~ 300 mAh/g, which is two times higher than that of the currently used $LiCoO_2$ cathode.
- Surface modification decreases irreversible capacity loss and increases discharge capacity due to suppression of oxygen vacancy elimination.
- Irreversible capacity loss can be completely eliminated by blending the layered oxide with a lithium-free host like V_2O_5.
- Surface modification with double layers (Al_2O_3 + $AlPO_4$ or Al_2O_3 + RuO_2) increases the rate capability significantly due to the suppression of SEI layer thickness and facilitation of electronic and ionic transfer channels.
- Morphology and electrochemical performances are influenced by the synthesis method. Carbonate precursor method has the potential to increase the tap density.

ACKNOWLEDGMENT